Influence of Bisolute Competition on the Desorption Kinetics of Polycyclic Aromatic Hydrocarbons in Soil

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The dual-mode (partition/hole-filling) model of soil organic matter (SOM) as a heterogeneous polymerlike sorbent of hydrophobic compounds predicts that a competing solute will accelerate diffusion of the primary solute by blocking the holes, allowing the principal solute to move faster through the SOM matrix. We tested this hypothesis with phenanthrene as the primary solute and pyrene as the competing solute in two sterile soils of widely different organic carbon content (1.4 and 43.9%). Two- and 33-d isotherms of phenanthrene in both soils were nonlinear, indicating a heterogeneous distribution of sites. Pyrene suppressed phenanthrene sorption and increased the linearity of its isotherm. Uptake (adsorption) rates were measured in batch systems after preincubating with pyrene. Desorption was measured by the sequential dilution technique at constant pyrene concentration in the supernatant. The design of the experiment precluded comparison of adsorption rates, but desorption rates increased significantly (but not dramatically) as a function of pyrene concentration. Moreover, the effect was noticeable even at low and roughly equimolar concentrations of the two compounds ($\sim$0.5 μmol/gOC). The effect was qualitatively similar in the two soils, implicating SOM as the matrix in which the effect takes place. The results suggest that the competing solute excludes the primary solute from less mobile sorption domains in SOM. Interpreted according to the polymer model, this exclusion is postulated to occur by a "hole-plugging" (competitive displacement) mechanism possibly in concert with penetrant-induced plasticization of SOM which leads to destruction of holes.

Introduction

The sorption of hydrophobic compounds to natural solids is the dominant factor controlling their transport, biodegradation, and toxicity. The study of sorptive interactions between compounds is essential given the prevalence of sites in the environment where multiple contaminants coexist. The competitive sorption of charged or polar contaminants to specific binding sites within soil has been known for some time. Zachara et al. (*1*) described the competitive sorption of protonated aromatic heterocyclic compounds in soil and suggested that competitive effects among ionized compounds

may significantly influence their transport in groundwater. Boyd (*2*) described the hydrogen-bonding of substituted phenols to soil and observed that the sorption of any one compound was reduced by the presence of a second compound. Conversely, Chiou et al. (*3*) did not observe competitive effects in the sorption of certain nonionic aromatic compounds to soil. However, other studies since have demonstrated competitive sorption between nonpolar or weakly polar compounds including halogenated aliphatics (*4–7*), substituted benzenes (*8*), and polycyclic aromatic hydrocarbons (*9–11*) and between pollutants (1,3-dichlorobenzene, 2,4-dichlorophenol) and naturally occurring aromatic acids (*12*). Recently we showed that one compound may increase the biological availability of another by competitive displacement (*10, 11*).

Soil organic matter (SOM) is usually the principal sorbing component of hydrophobic contaminants in soils and sediments. The modern paradigm of SOM is a random three-dimensional network phase consisting of humic and remnant-biologic macromolecules. We have regarded this material to consist of flexible "rubbery" phases and inflexible "glassy" phases analogous to the same states that may be assumed by a polymer (*5, 13*). A characteristic feature of the glassy state is the presence of unrelaxed free-volume in the form of internal nanometer-size voids or pores. Such pores have been detected in natural organic matter from a variety of sources (*5, 14*). Sorption in rubbery domains occurs by solid-phase dissolution (partition), which is linear with concentration and noncompetitive, while sorption in glassy domains occurs by a dual-mode mechanism that includes both partition and adsorption-like ("hole-filling") interactions and is nonlinear. In multisolute systems, competitive sorption will occur as the contaminants access a finite number of holes. Xing and Pignatello (*5*) studied the sorption of chlorinated benzenes to SOM materials and found correlations between nanoporosity and the degree of nonlinearity in single-solute systems and the degree of competitive sorption in bisolute systems. Independently, Weber and co-workers (*6, 7, 15–17*) have accumulated data in support of a heterogeneous "hard"/"soft" model of SOM—the Dual Reactive Domain Model—that accounts for nonideal sorption behavior.

A prediction of the rubbery/glassy model is that the rate of sorption will be affected by the presence of a cosolute. From studies of diffusion in polymers it is known that the mobility of molecules in holes is substantially lower than the mobility of molecules in the dissolution domain (*18, 19*). Likewise, molecules diffusing through the SOM pseudophase will be momentarily held up by adsorption in holes of the glassy regions. The cosolute will occupy a fraction of these holes, depending on its concentration. At high concentrations the cosolute may convert the glassy polymer to a rubbery polymer by a softening or "plasticization" effect. This will also serve to increase the diffusivity of the principal solute, since diffusivities in rubbery polymers are generally much greater than in glassy polymers (*18*). Thus, the cosolute is expected to increase the rate of sorption and desorption of the principal solute in relation to its concentration. In an earlier study, White et al. (*11*) found that phenanthrene and pyrene were competitive in a high-organic soil. In the present study we test the hypothesis that plugging the holes with pyrene will lead to enhanced rate of transport of phenanthrene through SOM. To determine whether such a phenomenon as this takes place in SOM, we compared a mineral soil with little SOM (1.4% OC) to a high-organic soil with little mineral phase (6.9% ash).

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Experimental Section

Materials. The soils used were Cheshire fine sandy loam (1.4% organic carbon, OC) from Hamden, CT, and Pahokee peat (43.9%; 6.9% ash), a reference material from the International Humic Substances Society (Department of Soil Science, University of Minnesota). The peat properties are reported elsewhere (5, 13). The loam was air-dried and passed through a 2-mm sieve. The peat was received dry and passed through a 0.5-mm sieve. Both soils were sterilized with 2.5 Mrad of γ-radiation from a ^{60}Co source (Ward Laboratories, Cornell University, Ithaca, NY). [9-^{14}C]Phenanthrene (>98% purity, 46.9 mCi/mmol) and [4,5,9,10-^{14}C]-pyrene (>98% purity, 58.7 mCi/mmol) were purchased from Sigma Chemical Co. (St. Louis, MO). Unlabeled phenanthrene and pyrene were also purchased from Sigma. On anticipation that these results would relate to planned biodegradation studies, the aqueous phase for all experiments was an inorganic salts solution that contained 0.1 g of CaCl$_2$·2H$_2$O, 0.1 g of NH$_4$NO$_3$, 0.049 g of MgSO$_4$, 0.2 g of KH$_2$PO$_4$, 0.8 g of K$_2$HPO$_4$, and 0.01 g of FeCl$_3$ per liter of distilled water. In all experiments, NaN$_3$ (0.2 g/L) was added to maintain sterility. The pH of the salts solution was 7.1. All water used had been distilled and passed through a Barnsted Nanopure (ion-exchange and activated carbon) purification system.

Sampling and Analysis. To ensure that a random particle size distribution was delivered to individual replicate bottles, samples of loam and peat were moistened with distilled water (10% and 45% w/w, respectively) prior to weighing. Indicated amounts of soil for individual experiments refer to the air-dry weight. Moisture contents were 0.015 (loam) and 0.11 (peat) g water per g oven-dry soil, respectively. For all experiments, suspensions of loam or peat received predetermined amounts of ^{14}C-phenanthrene, ^{14}C-pyrene, or unlabeled PAH in methanol carrier of volume less than 0.1% of the total aqueous volume. The volume of methanol was kept constant among all samples and controls. Bottles were mixed end-over-end at 21 °C on Rugged Rotator shakers (Glas Col, Terre Haute, IN) operating at 15 rpm. To determine solution PAH concentration, replicates were centrifuged at 750g for 20-min (loam) or 30-min (peat) on a bucket centrifuge, a portion of the supernatant removed, and the radioactivity measured by liquid scintillation counting.

In some experiments, phenanthrene was determined by gas chromatography (GC). Samples were extracted with dichloromethane containing an internal standard of naphthalene (25 mg/L). The organic phase (2 μL) was injected onto a PTE5 fused silica capillary GC-column (Supelco, Bellefonte, PA) and detected with a flame ionization detector (FID). The injector and detector temperatures were 290 °C and 300 °C, respectively. An initial temperature of 40 °C was maintained for 3 min and then was increased by 20 °C per min to 280 °C. The final temperature was maintained for a minimum of 2 min. The retention time of phenanthrene was 14.7 min.

Extraction of solids (≤200 mg) to determine mass balance was carried out in 10–15 mL methanol at 70 °C for 4 h.

Effect Nonsettling Organic Matter. Schrap et al. (20) found that the apparent solubility of hexachlorobenzene and two polychlorinated biphenyls was increased up to 8-fold due to the presence of nonsettling organic matter (colloidal plus "dissolved" organic matter) from sediments. We sought to investigate the effect of nonsettling organic carbon from the supernatant of suspensions of each soil on the apparent solubility of phenanthrene in order to validate the method of direct sampling of the aqueous phase to determine sorbed solute concentrations. Samples of loam (11.4 g, 150 mL) and peat (0.45 g, 150 mL) were prepared in 160-mL crimp-cap serum bottles and were shaken for 72 h. These soil:water
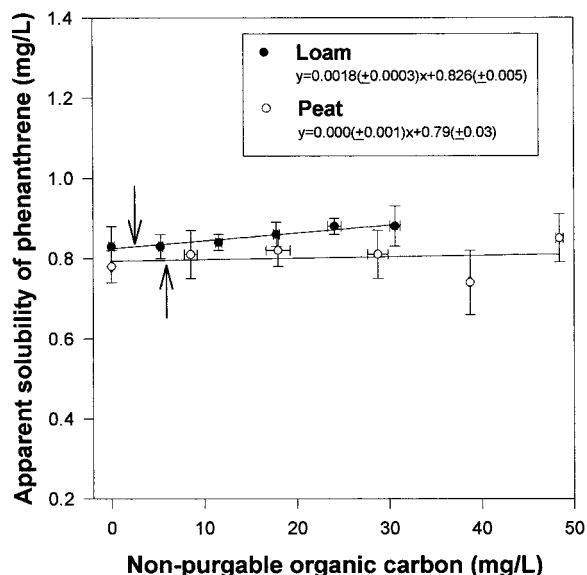

FIGURE 1. The influence of nonsettling organic matter on the apparent solubility of phenanthrene in water at 21 °C. Error bars represent standard deviation of five replicate determinations. The arrows indicate the concentration of nonsettling organic matter present in all further experiments.

ratios are about 10 times greater than those used in all other experiments. The bottles were centrifuged, and the supernatant with accompanying nonsettling organic matter was removed by pipet. A dilution series of the supernatant was created (100, 80, 60, 40, 20, and 0% supernatant) using Nanopure water. For each member of the dilution series, a portion was analyzed for nonpurgeable organic carbon (NPOC) (Shimadzu TOC 5000, Shimadzu Corp., Kyoto, Japan) using potassium hydrogen phthalate standards. Other portions were transferred to 35-mL glass vials with Teflon inserts and amended with 40 mg of phenanthrene per 30-mL portion (five replicates). The vials were shaken for an additional 7 d at 21 °C. All vials were then centrifuged at 420g, and the supernatant was removed by pipet. The supernatant was passed through a disposable pipet (Fisher Scientific, catalogue no. 13-678-20D) packed with a small plug of glass wool in the narrow section to remove any crystals of phenanthrene, and the filtrate was collected after rejecting the first ~1.0 mL. Each filtrate was shaken overnight with 5 mL of CH$_2$Cl$_2$. An aliquot of the organic phase was then analyzed by gas chromatography (GC) to determine the concentration of phenanthrene. Infrequently, a sample would show an unexpectedly very high assay; this was attributed to penetration of the filter by small phenanthrene crystals and was therefore rejected.

In controls with mineral salts solution free of organic matter, the solubility of phenanthrene averaged 0.78 ± 0.04 and 0.83 ± 0.05 mg/L (Figure 1), close to the reported phenanthrene solubility in water (21). As indicated by the slope of the regression line for each soil, the effect of the nonsettling organic matter on the apparent solubility of phenanthrene was negligible, especially at NPOC concentrations present in the aqueous phase in subsequent sorption and desorption experiments (indicated by the arrows). In the presence of the maximum NPOC—30.6 or 48.4 mg/L from suspensions of loam or peat, respectively—the apparent solubility of phenanthrene was 0.88 and 0.85 mg/L, respectively, insignificantly different from the controls ($p < 0.05$). These data are consistent with those of Villholth (22), who was unable to detect PAH partitioning to nonsettling organic matter if the solute log K_{ow} was less than 5.7 (phenanthrene $K_{ow} = 4.6$). Therefore, in all sorption experiments, we may

neglect the effect of nonsettling organic matter on aqueous phenanthrene determinations.

Thermodynamic Experiments. *Effect of Variable Pyrene Concentration on Single-Point Phenanthrene Sorption.* Samples of loam (0.11 g, 13 mL) and peat (0.02 g, 50 mL) were amended with phenanthrene at initial rates of 171 μg/g OC (1.5 $\times$ 10^5 disintegrations per minute, dpm) and 52.2 μg/g OC (2.7 $\times$ 10^5 dpm), respectively. Pyrene was then added to both soils at various initial concentrations: 85.7−10 100 μg/g OC for the loam and 42.6−6200 μg/g OC for the peat. At 14 d, the amount of phenanthrene present in solution was determined by liquid scintillation counting. Using identical conditions, the amount of pyrene sorbed at the aforementioned concentrations was determined in each soil by constructing 14-d sorption isotherms for pyrene (corrected for the effect of nonsettling organic matter in the same manner as phenanthrene) in the presence of the appropriate amount of phenanthrene.

Effect of Constant Pyrene Concentration on Phenanthrene Isotherms. Samples of loam (0.11 g, 13 mL) and peat (0.02 g, 50 mL) were prepared in 15-mL serum vials and 50-mL glass centrifuge tubes, respectively. The samples received identical amounts of ^{14}C-phenanthrene: loam, 0.07 μg (4.1 $\times$ 10^4 dpm); peat, 0.43 μg (2.5 $\times$ 10^5 dpm). Replicates then received appropriate amounts of unlabeled phenanthrene to yield the desired concentration. In addition, half the samples of each soil received 0.58 mg (loam) or 0.12 mg (peat) of pyrene per liter of solution. The amount of radioactivity in solution was determined at 2 and 33 d as already described. The recoveries of phenanthrene and pyrene by solvent extraction at termination averaged 97.7 $\pm$ 1.8% and 99.0 $\pm$ 1.1%, respectively.

Kinetic Experiments. Samples of loam (0.28 g, 37.0 mL) and peat (0.02 g, 50 mL) were prepared in 40- and 50-mL screw cap glass vials fitted with Teflon-lined inserts. The samples were amended with various concentrations of pyrene (0−4840 μg/g OC in the loam; 0−2850 μg/g OC in the peat). In addition, 1-L stock bottles containing the same soil:water ratio were prepared and amended separately with the same corresponding concentrations of pyrene. The stock supernatant was to be used later for the desorption part of the experiment as replacement fluid. After 14 d of shaking, the loam samples received 78.6 μg (short-term experiments) or 100 μg (long term) of phenanthrene per g OC (1.8−2.4 $\times$ 10^5 dpm), and the peat samples received 56.5 μg (short term) or 72.7 μg (long term) of phenanthrene per g OC (3.6−3.8 $\times$ 10^5 dpm). The uptake of phenanthrene was followed during 2 or 42 d periods in the loam and 2- or 76-d periods in the peat. After the appropriate uptake time, the stock bottles were centrifuged in 250-mL portions at 750g. The supernatant was removed by pipet and stored separately. At 2, 42, or 76 d, the samples were centrifuged, and approximately 90% of the supernatant was removed by pipet from each vial and replaced with an equal volume of supernatant from the stock bottles containing the appropriate amount of pyrene. Samples were then resealed and placed back on the shaker. Consecutive desorptions were thus conducted on individual samples at selected intervals.

Results

Thermodynamic Experiments. Figure 2 shows the effect of varying concentrations of pyrene on the 14-d single point apparent soil−water distribution ratio of phenanthrene normalized to organic carbon, K_{oc}^{app} (14 d). The K_{oc}^{app} [L/kg] is defined as

$$K_{oc}^{app} = \frac{q}{C}\frac{1}{f_{oc}} \qquad (1)$$

where q is the sorbed concentration [mol/kg], C is the solution concentration [mol/L], and f_{oc} is the fraction of organic carbon
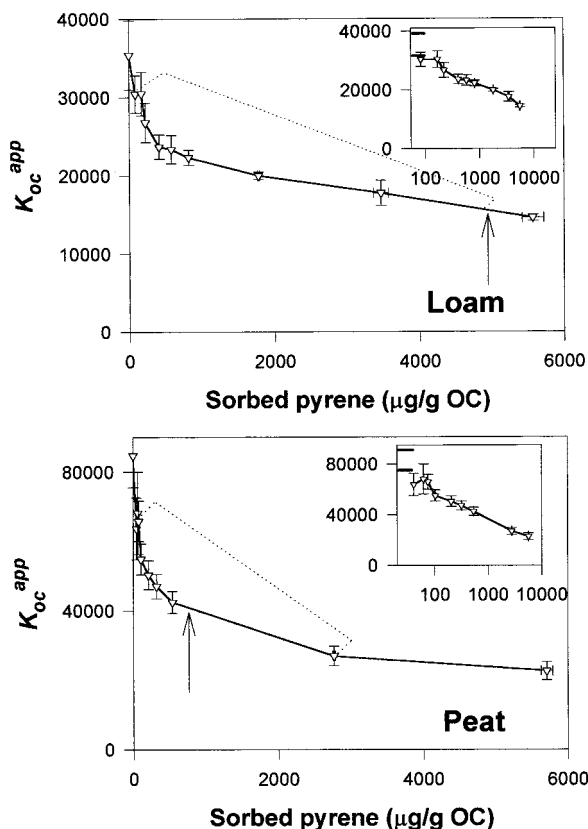

FIGURE 2. Effect of pyrene on the K_{oc} of phenanthrene after 14 d of equilibration in Cheshire fine sandy loam or Pahokee peat. Arrows indicate concentrations of pyrene present in phenanthrene isotherms (Table 1). Brackets represent range of pyrene concentrations used in the kinetic experiments. Phenanthrene concentration in the zero-pyrene samples was 52.2 μg/g OC for the loam and 171 μg/g OC for the peat. At the concentrations of pyrene tested, 83−98% of the pyrene initially added was sorbed to the loam, and, in the peat, 76−96% was sorbed. Insets are the same data plotted on log scale; the bars signify the range in the zero-pyrene samples. K_{toc}^{app} and sorbed pyrene values were based on air-dry weight of soil (see Experimental Section).

of the soil. In both soils, the steepest reduction in K_{oc}^{app} (14 d) occurred at the lower concentrations of pyrene, and the competitive effect leveled off as the amount of pyrene increased. Interestingly, the competitive effect was observable even at sorbed concentrations of pyrene that were comparable to that of phenanthrene. For example, in the loam, 0.56 μmol/g OC of pyrene reduced the K_{oc}^{app} (14 d) of 0.60 μmol/g OC of phenanthrene by 14%. Similarly, in the peat, 0.30 μmol/g OC of pyrene reduced the K_{oc}^{app} of 0.40 μmol/g OC of phenanthrene by 25%. In each case, the difference was significant at $p < 0.05$. A maximum of 58% and 73% reductions in the K_{oc}^{app} (14 d) of phenanthrene was obtained for the loam and peat, respectively.

Two- and 33-d isotherms of phenanthrene were constructed in the loam and peat in the presence or absence of pyrene. Pyrene was added to each soil at the respective concentration indicated by the arrows in Figure 2 (always below its water solubility). The phenanthrene data were fit to the Freundlich equation

$$q = K_F C^N \qquad (2)$$

where N [dimensionless] and K_F [$(\mu$g/g$)(\mu$g/mL$)^{-N}$] are the Freundlich exponential and preexponential fitting parameters. The results are given in Table 1. All isotherms are nonlinear ($N < 1$). The linearity tends to decrease with contact

TABLE 1. Freundlich Parameters for Phenanthrene in Two Soils in the Presence or Absence of Pyrene at Different Contact Times

equil time (d)	pyrene added (µg/g OC)	no. of data, n	log K_F[a]	N[a]	r^2	MSWE[b]
			Cheshire Fine Sandy Loam			
2	0	15	3.99 (3.92−4.08)	0.835 (0.795−0.875)	0.994	0.017
2	4840	15	3.95 (3.90−4.00)	0.924 (0.894−0.954)	0.997	0.007
33	0	15	4.10 (3.99−4.21)	0.821 (0.768−0.874)	0.989	0.035
33	4840	15	4.18 (4.11−4.26)	0.960 (0.922−0.998)	0.996	0.011
			Pahokee Peat			
2	0	15	4.00 (3.94−4.05)	0.784 (0.760−0.808)	0.997	0.006
2	684	15	3.97 (3.90−4.05)	0.845 (0.807−0.882)	0.995	0.012
33	0	15	4.20 (4.15−4.25)	0.766 (0.747−0.786)	0.998	0.005
33	684	15	4.27 (4.19−4.35)	0.859 (0.825−0.893)	0.996	0.010

[a] 95% confidence interval. Log K_F values were based on air-dry weight of soil (see Experimental Section). [b] Mean weighted standard error: $1/(n − 2)\Sigma[(q − q_{calc})^2/q^2]$.
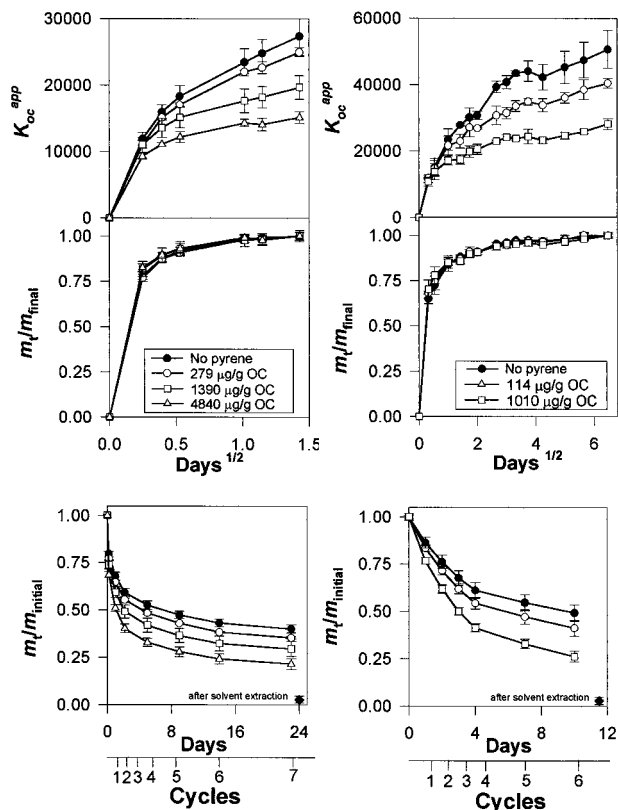
FIGURE 3. Effect of pyrene on adsorption and desorption of 2- and 42-d aged phenanthrene in Cheshire fine sandy loam. The m_{final} refers to the final mass taken up by the solid just prior to desorption, and this value ranged from about 60 to about 85% of mass added; $m_{initial}$ refers to the initial mass present on the solids and is equal to m_{final}. The panels on the left refer to short-term experiments; those on the right are long-term. K_{oc}^{app} values were based on air-dry weight of soil (see Experimental Section).

time as observed previously for phenanthrene (23) and for other compounds (13), but the differences in N were not statistically significant at $p < 0.05$ in any case. The presence of 4840 µg/g OC of pyrene in the loam and 683 µg/g OC of
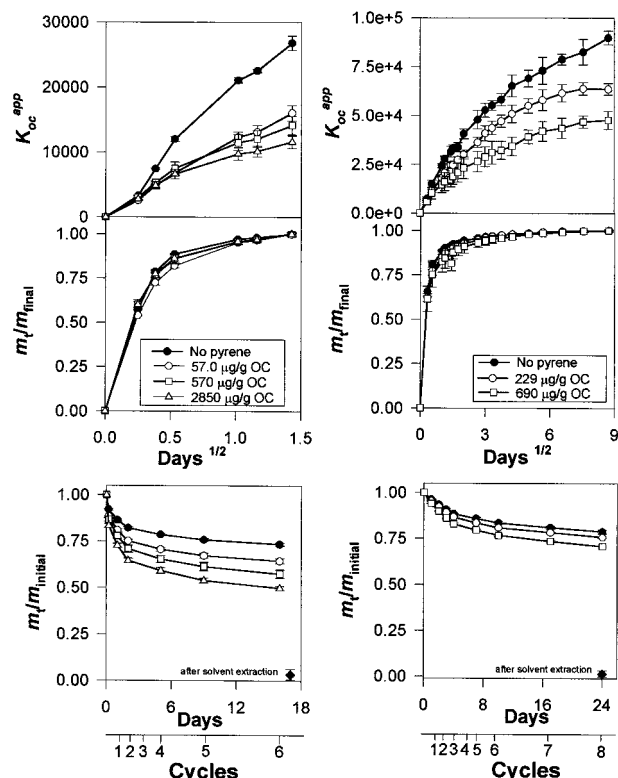
FIGURE 4. Effect of pyrene on adsorption and desorption of 2- and 76-d aged phenanthrene in Pahokee peat. The m_{final} refers to the final mass taken up by the solid just prior to desorption, and this value ranged from about 75 to about 90% of mass added; $m_{initial}$ refers to the initial mass present on the solids and is equal to m_{final}. The panels on the left refer to short-term experiments; those on the right are long-term. K_{oc}^{app} values were based on air-dry weight of soil (see Experimental Section).

pyrene in the peat significantly ($p < 0.01$) increased the linearity of both the 2- and 33-d isotherms of phenanthrene. In addition, in the presence of pyrene there was a trend of increasing linearity with contact time, suggesting a continuing competitive effect, but the differences in N were not statistically significant at $p < 0.05$.

Kinetic Experiments. The effect of pyrene on phenanthrene sorption kinetics in the loam (Figure 3) and peat (Figure 4) were determined in separately conducted experiments of "short term" (left side graphs) and "long term" (right side graphs). The soils were allowed to equilibrate with pyrene for 14 d prior to addition of phenanthrene, the amount of which was the same for every vial in each experiment. Adsorption was monitored by sampling the solution phase periodically. Desorption was conducted by the sequential dilution method. The replacement fluid at each step was the supernatant from a soil−water suspension that had been spiked with pyrene, but not phenanthrene, and handled identically as the sample. This procedure ensured that pyrene concentration and other water chemistry would remain approximately constant during phenanthrene desorption.

The top graphs of Figures 3 and 4 show $K_{oc}^{app}(t)$ during the adsorption phase. Once again, the competitive effect is apparent in these plots. The $K_{oc}^{app}(t)$ was reduced by a maximum of 45% in the loam and 57% in the peat by pyrene (Table 2). Detectable effects on $K_{oc}^{app}(t)$ can be seen even at comparable concentrations of phenanthrene and pyrene (0.60 and 0.56 µmol/g OC in the loam; 0.40 and 0.30 µmol/g OC in the peat).

The middle graphs of Figures 3 and 4 follow m_t/m_{final}—an index of adsorption expressing cumulative mass relative to

TABLE 2. Effect of Pyrene at Different Concentrations on Phenanthrene Sorption and Desorption in Cheshire Fine Sandy Loam and Pahokee Peat[c]

duration of uptake (d)	pyrene added (μg/g OC)	% final reduction in $K_{oc}(t)$[a]	normalized initial rate of desorption (d^{-1})[a]	final phenanthrene desorbed (% of initial)[a]
2	0		1.04 A	60 A
2	279	8.7 A	1.15 A[b]	65 B
2	1390	28 B	1.32 B	71 B[b]
2	4840	45 C	1.59 C	79 C
42	0		0.116 E	51 E
42	114	20 E	0.136 F	58 E[b]
42	1010	44 F	0.176 G	74 F
2	0		0.394 A	27 A
2	57.0	40 A	0.586 B	36 B
2	570	47 A	0.677 C	43 C
2	2850	57 B	0.838 D	50 D
76	0		0.038 E	21 E
76	229	29 E	0.047 F	24 F
76	690	47 F	0.060 G	29 G

[a] Within columns of soil type and for the same duration of uptake, values followed by the same letter are not significantly different at the 95% or better confidence level. [b] This value and the one immediately above it in the same column are significantly different at 90% confidence level, however. [c] Initial rates were calculated as mass desorbed within time of first sample. The amount of pyrene added is based on air-dry weight of soil (see Experimental Section).

final mass just prior to the desorption phase—with time ($t^{1/2}$). This index is often used in diffusion studies, although for nonlinear uptake in a finite bath it cannot be taken as an exact measure of the degree of equilibrium (24). The adsorption plots show no significant *apparent* trend in m_t/m_{final} as a function of pyrene concentration (see Discussion section). The bottom graphs of Figures 3 and 4 show desorption curves plotted as $m_t/m_{initial}$ vs t and the desorption cycle number, where $m_{initial}$ is the initial phenanthrene mass sorbed at the beginning of the desorption phase equal to m_{final} of the adsorption phase. In contrast to adsorption, competitive effects on phenanthrene desorption are clearly and consistently visible in the graphs. The normalized initial rate of desorption [d^{-1}, first time point] increased significantly with increasing concentration of pyrene, as did the final percent of initial sorbed concentration (Table 2). Comparing the short- and long-term experiments at the same pyrene concentration, both the initial rate and final extent of desorption for both soils declined with increased sorption ("aging") time, in keeping with a previous study (25). Solvent extraction recoveries of phenanthrene after the experiment succeeded in closing mass balance in all cases, as noted in Figures 3 and 4.

Discussion

This is the first published study to our knowledge showing that cosolutes may affect the rates as well as the position of equilibrium of the principal solute in SOM. In the past we have attributed the thermodynamic competitive effect to the presence of a glassy component in SOM, which is conceptualized as a heterogeneous, random network macromolecular phase with "polymer-like" properties. The kinetic results described in this study are consistent with this interpretation, and we continue to use the polymer concept as our working hypothesis.

It is reasonable to conclude that the competitive effect operates within the organic domain of the soil and that the SOM of the two soils is qualitatively similar. The two soils have markedly different OC contents, yet behave analogously in these experiments which argues in favor of a common mechanism. The peat has so little mineral matter (6.9% ash) that in terms of its sorbent properties it may be considered completely organic. In a previous study of 1,3-dichloroben-

zene sorption by the peat (5), removal of the mineral component with HF had no effect on the nonlinearity (*N* value) and actually increased the K_F slightly. In addition, highly hydrophobic compounds have practically no affinity for mineral surfaces in the presence of organic matter (26). The isotherms of phenanthrene are slightly more linear, and the thermodynamic competitive effect is somewhat weaker, in the Cheshire loam compared to the peat. This indicates that the loam SOM has a smaller hole-filling domain for phenanthrene than does the peat. The slower overall rates in the peat probably reflect the larger dimensions of SOM phases in this soil compared to the loam: i.e., the peat is characterized by macroscopic SOM particles, while the loam (97% mineral) is likely characterized by coatings and patches of SOM on the mineral surface.

The results of the thermodynamic experiments are in keeping with our previous studies which point to the polymer model of SOM. The isotherms of phenanthrene in both soils are nonlinear, with Freundlich exponents ranging from 0.821 to 0.835 in the loam and from 0.766 to 0.784 in the peat, depending on the time of equilibration. Addition of progressively higher pyrene concentrations to suspensions containing a constant amount of phenanthrene resulted in increasing suppression of phenanthrene sorption until a nearly constant level was reached (Figure 2). It is hypothesized that the competitive effect is a result of cosolute molecules vying for a limited number of discrete holes within the glassy regions of SOM. The presence of pyrene increased the linearity of the phenanthrene isotherms (*N* values of 0.924−0.960 for the loam and 0.845−0.859 for the peat). Such effects have been observed before (5, 12, 27) and have been interpreted to indicate that the principal solute is more and more restricted to the dissolution domains of SOM with increasing cosolute concentration.

The cosolute influence on rates in terms of this polymer model can be explained as follows. Pyrene occupies a fraction of holes ordinarily accessible to phenanthrene. With fewer and fewer holes available to phenanthrene, its passage through SOM is more and more diverted to the dissolution domains of the rubbery and glassy states where diffusion is faster. This is in essence a hole plugging mechanism. Diffusion generally is more hindered in the glassy state than the rubbery state of organic solids due to the difference in viscosity. Berens (18) found that the diffusion coefficients for small organic molecules are several orders of magnitude smaller in glassy poly(vinyl chloride) than in the same polymer "plasticized" to a rubbery state with a phthalate ester. In addition, holes present in the glassy state serve to restrict the mobility of molecules (18, 19, 27). This is evident from the work of Cain et al. (19) who studied diffusion of CO_2 in glassy polycarbonate by ^{13}C NMR. They calculated dissolution−dissolution, dissolution−hole, and hole−hole diffusion coefficients of 1.53×10^{-7}, 4.5×10^{-9}, and 1.94×10^{-13} cm^2 s^{-1}, respectively, at 300 K. The divergence of these values is expected to be amplified as penetrant size increases (19). Vieth and Sladek (28) modeled diffusion through glassy polymers as occurring exclusively in the dissolution domain, with holes providing local traps for immobilizing molecules. Chang et al. (29) found the diffusion coefficients of toluene, *n*-hexane, and acetone in pressed humic acid disks to be around $10^{-8}-10^{-9}$ cm^2 s^{-1}, which is more in line with values found in rubbery polymers. However, reconstituted humic acid solids represent a more rubbery form of natural organic matter than the original SOM that served as its source (5, 25).

Besides hole plugging is the possibility that penetrants influence the bulk properties of SOM. Huang and Weber (30) report that a high concentration of phenanthrene may reach sorptive equilibrium more quickly than a low concentration and suggest this is due to a softening effect in which local regions of SOM are converted to rubbery forms by solute

penetration. The softening of synthetic glassy polymers by penetrants is well-known. The effect of plasticizers on PVC mentioned above (*19*) exemplifies it. In studies of CO_2 and small hydrocarbon sorption in polymer films, Kamiya and co-workers (*31*) observed penetrant-induced glassy-to-rubbery phase changes well below the glass-transition temperature, T_g. The isothermal "glass-transition concentration" (C_g), which depended on polymer and penetrant, corresponded to simultaneous abrupt changes in the following: the dilation (swelling) curve, the curvature in the sorption isotherm, and (for propane) the curve of the concentration dependence of the diffusion coefficient. These authors proposed that penetrant molecules present in both holes and dissolution domain sites were capable of "dissolving" the holes by relaxing the local polymer structure at some threshold concentration different for each domain. In the soils of Huang and Weber (*30*) showing the clearest effects, the average phenanthrene concentrations compared at final uptake were approximately 300 vs 7500 μg (g OC)$^{-1}$ (EPA-23 soil) and 12 500 vs 100 000 μg (g OC)$^{-1}$ (Lachine shale). In our experiments, the lowest concentrations of pyrene giving observable effects on phenanthrene kinetics were 114 μg (g OC)$^{-1}$ (Cheshire loam) and 57 μg (g OC)$^{-1}$ (Pahokee peat). The corresponding initial sorbed phenanthrene concentrations were comparable, bringing the total initial PAH present in the soil to <200 μg (g OC)$^{-1}$. While the total is *less* than the lower of the phenanthrene concentrations tested by Huang and Weber (*30*), it is possible that locally higher concentrations existed under the nonequilibrium conditions. Whether or not PAH concentrations at any time were above C_g, and thus able to influence mass transfer rates via plasticization, is unknown; if so, plasticization would act in concert with hole plugging to increase the diffusivity of phenanthrene.

A noteworthy observation of the present study is that the competitive effect on phenathrene desorption rates can be seen at short times (hours). If the competitive domain consists of holes in glassy SOM, this means that some fraction of the glassy phase is close in proximity to the bulk solution. The competitive effect between geometrical isomers of dichlorobenzenes in glassy poly(vinyl chloride) microspheres is quite evident (*5*) even at short times relative to equilibrium (*13*). The continuing trend toward increasing linearity of phenanthrene sorption with time in the presence of pyrene (the opposite trend occurs in its absence) suggests that competitive effects are experienced by more slowly penetrating molecules, as well. We note that sorption times used in the kinetic experiments (14 day prior incubation with pyrene; the phenanthrene uptake periods shown in Figures 3 and 4) are not long enough for pyrene nor phenanthrene to come to full equilibrium (more than 100 days are required). Thus, we are biased in these experiments toward viewing the comparatively short-term behavior.

The weak or negligible apparent competitive affect on rates of adsorption compared to desorption is not unexpected if one considers the following two possible causes. The first is related to experimental design. Given its short preequilibration time (14 d) and expected slower rate of diffusion (larger size, greater hydrophobicity), pyrene probably had not penetrated very far into the organic matter by the time phenanthrene was introduced. It is possible that a fraction of phenanthrene overtook pyrene spatially and behaved as a single solute. By the time desorption commenced, however, pyrene had much more time to penetrate the organic phase and exert its competitive effect. The second reason has to do with the inherent asymmetry of sorption/desorption rates in nonlinear systems, where the diffusion coefficient is concentration dependent. (Here, pyrene serves to alleviate the concentration dependence by blocking/eliminating holes and linearizing the isotherm). It is predicted and observed

that adsorption and desorption curves coincide when the isotherm is linear but that desorption becomes increasingly slower than adsorption as linearity decreases (*32*). It follows that desorption will be more sensitive to changes in linearity brought about by competitive effects. Thus, for example, adsorption curves for solutes having Freundlich exponents N of 1.0 verses 0.75 are not very distinguishable, while desorption curves are much more clearly so (*32*). In our case, we expect the competitive effect to be magnified for desorption. This was verified by hypothetical simulations using a dual-mode diffusion model for polymers (*28*) modified to take into account competitive Langmuir sorption. This model (to be presented elsewhere) showed that, for a competitive desorption effect comparable in magnitude to those observed here, the corresponding competitive adsorption effect was subtle and likely difficult to detect without intensive and highly precise data.

The results show that the competing solute excludes the primary solute from less mobile sorption domains in SOM. While this behavior is consistent with the polymer model of SOM, it may not exclude the presence of other as-yet-unknown sorbent materials or phases that have a high affinity for PAHs, provided both soils contain them and provided they have "slower sites" that are blocked or eliminated by the cosolute.

The findings presented in this paper are important because they show that the kinetics of desorption of a single solute may be significantly influenced by the presence of a competitor. This may have implications for solute transport and bioavailability. In addition, these results are in keeping with a heterogeneous view of SOM.

Acknowledgments

Literature Cited

(1) Zachara, J. M.; Ainsworth, C. C.; Cowan, C. E.; Thomas, B. L. *Environ. Sci. Technol.* **1987**, *21*, 397−402.

(2) Boyd, S. A. *Soil Sci.* **1982**, *134*, 337−343.

(3) Chiou, C. T. In *Organic Substances and Sediments in Water*; Baker, R. A., Ed.; Lewis Publishers: Chelsea, MI, 1991; Vol. 1, Chapter 1.

(4) Pignatello, J. J. In *Organic Substances and Sediments in Water*; Baker, R. A., Ed.; Lewis Publishers: Chelsea, MI, 1991; Vol. 1, Chapter 16.

(5) Xing, B.; Pignatello, J. J. *Environ. Sci. Technol.* **1997**, *31*, 792−799.

(6) McGinley, P. M.; Katz, L. E.; Weber, W. J., Jr. *Environ. Sci. Technol.* **1993**, *27*, 1524−1531.

(7) McGinley, P. M.; Katz, L. E.; Weber, W. J., Jr. *Water Resour. Res.* **1996**, *32*, 3571−3577.

(8) Stuart, B. J.; Bowlen, G. F.; Kosson, D. S. *Environ. Prog.* **1991**, *10*, 104−109.

(9) Abdul, A. S.; Gibson, T. L. *Hazard. Waste Hazard. Mater.* **1986**, *3*, 125−136.

(10) White, J. C.; Alexander, M.; Pignatello, J. J. *Environ. Toxicol. Chem.* **1999**, *18*, 182−187.

(11) White, J. C.; Hunter, M.; Pignatello, J. J.; Alexander, M. *Environ. Toxicol. Chem.* **1999**, *18*, 1728−1732.

(12) Xing, B.; Pignatello, J. J. *Environ. Sci. Technol.* **1998**, *32*, 614−619.

(13) Xing, B.; Pignatello, J. J. *Environ. Toxicol. Chem.* **1996**, *15*, 1282−1288.

(14) de Jonge, H.; Mittelmeijer-Hazeleger, M. C. *Environ. Sci. Technol.* **1996**, *30*, 408−413.

(15) Weber, W. J., Jr.; McGinley, P. M.; Katz, L. E. *Environ. Sci. Technol.* **1992**, *26*, 1955−1962.

(16) Huang, W.; Weber, W. J., Jr. *Environ. Sci. Technol.* **1997**, *31*, 2562−2569.

(17) Young, T. M.; Weber, W. J., Jr. *Environ. Sci. Technol.* **1995**, *29*, 92−97.

(18) Berens, A. *Makromol. Chem., Macromol. Symp.* **1989**, *29*, 95−108.

(19) Cain, E. J.; Wen, W. Y.; Jones, A. A.; Inglefield, P. T.; Cauley, B. J.; Bendler, J. T. *J. Polym.Sci.: Part B: Polym. Phys.* **1991**, *29*, 1009−1020.

(20) Schrap, S. M.; Haller, M.; Opperhuizen, A. *Environ. Toxicol. Chem.* **1995**, *14*, 219−228.

(21) Huang, W.; Weber, W. J., Jr. *Environ. Sci. Technol.* **1997**, *31*, 3238−3243.

(22) Villholth, K. G. *Environ. Sci. Technol.* **1999**, *33*, 691−699.

(23) Weber, W. J., Jr.; Huang, W. *Environ. Sci. Technol.* **1996**, *30*, 881−888.

(24) Pignatello, J. J.; Xing, B. *Environ. Sci. Technol.* **1999**, *33*, 2837−2838.

(25) White, J. C.; Hunter, M.; Nam, K.; Pignatello, J. J.; Alexander, M. *Environ. Toxicol. Chem.* **1999**, *18*, 1720−1727.

(26) Mader, B. T.; Goss, K.-U.; Eisenreich, S. J *Environ. Sci. Technol.* **1997**, *31*, 1079−1086.

(27) Xing, B.; Pignatello, J. J.; Gigliotti, B. *Environ. Sci. Technol.* **1996**, *30*, 2432−2440.

(28) Vieth, W. R.; Sladek, K. J. *J. Colloid Sci.* **1965**, *20*, 1014−1033.

(29) Chang, M.; Wu, S.; Chen, C. *Environ. Sci. Technol.* **1997**, *31*, 2307−2312.

(30) Huang, W.; Weber, W. J., Jr. *Environ. Sci. Technol.* **1998**, *32*, 3549−3555.

(31) Kamiya, Y.; Bourbon, D.; Mizoguchi, K.; Naito, Y. *Polym. J.* **1992**, *24*, 443−449.

(32) Lin, T.; Little, J. C.; Nazaroff, W. W. *Environ. Sci. Technol.* **1994**, *28*, 322−330.